The role of solvent cohesion in nonpolar solvation

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SUPPORTING INFORMATION

The Role of Solvent Cohesion in Nonpolar Solvation

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Figure S1. Determination of P_i for hexadecane by extrapolation from the data[S1] for other linear alkanes.

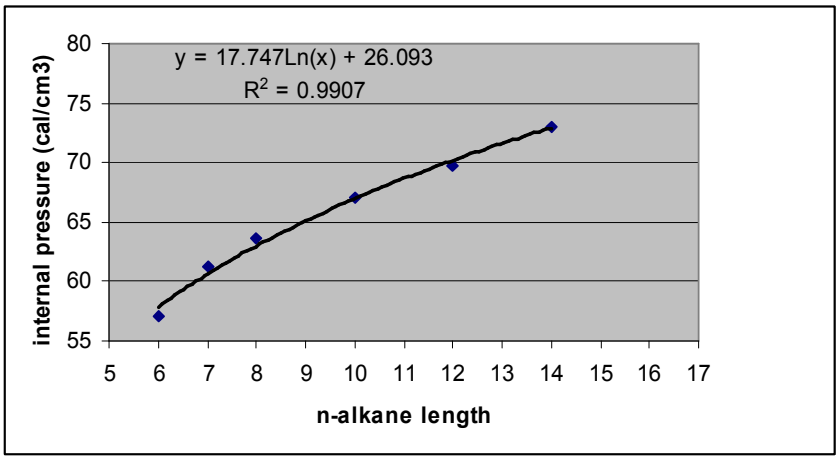


Table S1. Correlation coefficients (R^2) for plots of the Gibbs energy of transfer of a series of nonpolar solutes from the gas phase to a range of solvents versus solvent cohesion expressed as a linear combination of P_i and *ced* for different values of %*ced*. The last line shows the %*ced* for which the best correlation is obtained.

%*ced*	He	Ne	Ar	Kr	Xe	Rn	H2	Me	Et	Pr	Bu	Pen	Hex	Hep	Oct
10	0.576	0.581	0.639	0.485	0.345	0.346	0.672	0.467	0.361	0.281	0.257	0.197	0.264	0.276	0.186
20	0.672	0.734	0.87	0.905	0.845	0.877	0.844	0.799	0.743	0.688	0.672	0.653	0.667	0.682	0.624
30	0.573	0.649	0.835	0.926	0.94	0.845	0.774	0.895	0.89	0.884	0.874	0.875	0.873	0.88	0.852
40	0.501	0.578	0.762	0.892	0.943	0.959	0.689	0.89	0.922	0.945	0.939	0.948	0.942	0.943	0.934
50	0.454	0.531	0.701	0.861	0.93	0.962	0.642	0.861	0.918	0.956	0.953	0.968	0.959	0.958	0.96
60	0.422	0.499	0.656	0.835	0.918	0.962	0.578	0.831	0.905	0.951	0.951	0.971	0.957	0.955	0.966
70	0.4	0.476	0.621	0.815	0.907	0.961	0.544	0.804	0.89	0.942	0.944	0.968	0.949	0.947	0.965
80	0.383	0.458	0.595	0.8	0.898	0.961	0.518	0.781	0.877	0.931	0.935	0.962	0.94	0.938	0.961
90	0.371	0.445	0.574	0.788	0.89	0.96	0.498	0.762	0.854	0.921	0.927	0.957	0.931	0.929	0.957
best fit (% ced)	*16.3*	*17.5*	*22*	*26*	*35*	*55*	*19*	*33*	*45*	*50*	*53*	*58*	*53*	*52*	*63*

It appears that the %*ced* for the best fit seems to level off for the linear alkanes. This is most likely a result of the %*ced* approaching the limit for solvation of a methylene unit. It is also noteworthy that for these solutes the correlation coefficients show only minor changes in the range of 50-100 %*ced*. This is at least to some extent an artefact of the isolated position of water which allows it to exert a dominant influence on the linear regression analysis. Repeating the fitting procedure excluding the data for water gave clearer defined maxima in the relation between correlation coefficient and %ced. The position of the maxima is not significantly affected by excluding water.

Figure S2. Gibbs energies of transfer of the noble gases, hydrogen and linear alkanes from the gas phase to different solvents at 298 K as a function of solvent cohesion, as quantified a linear combination of the internal pressure (P_i) and the cohesive energy density (*ced*) (in cal/cm^3). Standard states: solute(ideal gas, 1M) → solute(ideal solution, 1M). The solvents include: n-hexadecane, n-decane, n-hexane, cyclohexane, carbontetrachloride, diethylether, toluene, benzene, ethyl acetate, methyl acetate, butanone, acetone, DMF, acetonitrile, propylene carbonate, DMSO, isobutyl alcohol, 1-butanol, 2-propanol, 1-propanol, ethanol, methanol, ethylene glycol and water. Data points for water are circled. The insets in the graphs of the smaller solutes show the corresponding correlations with *ced* only.

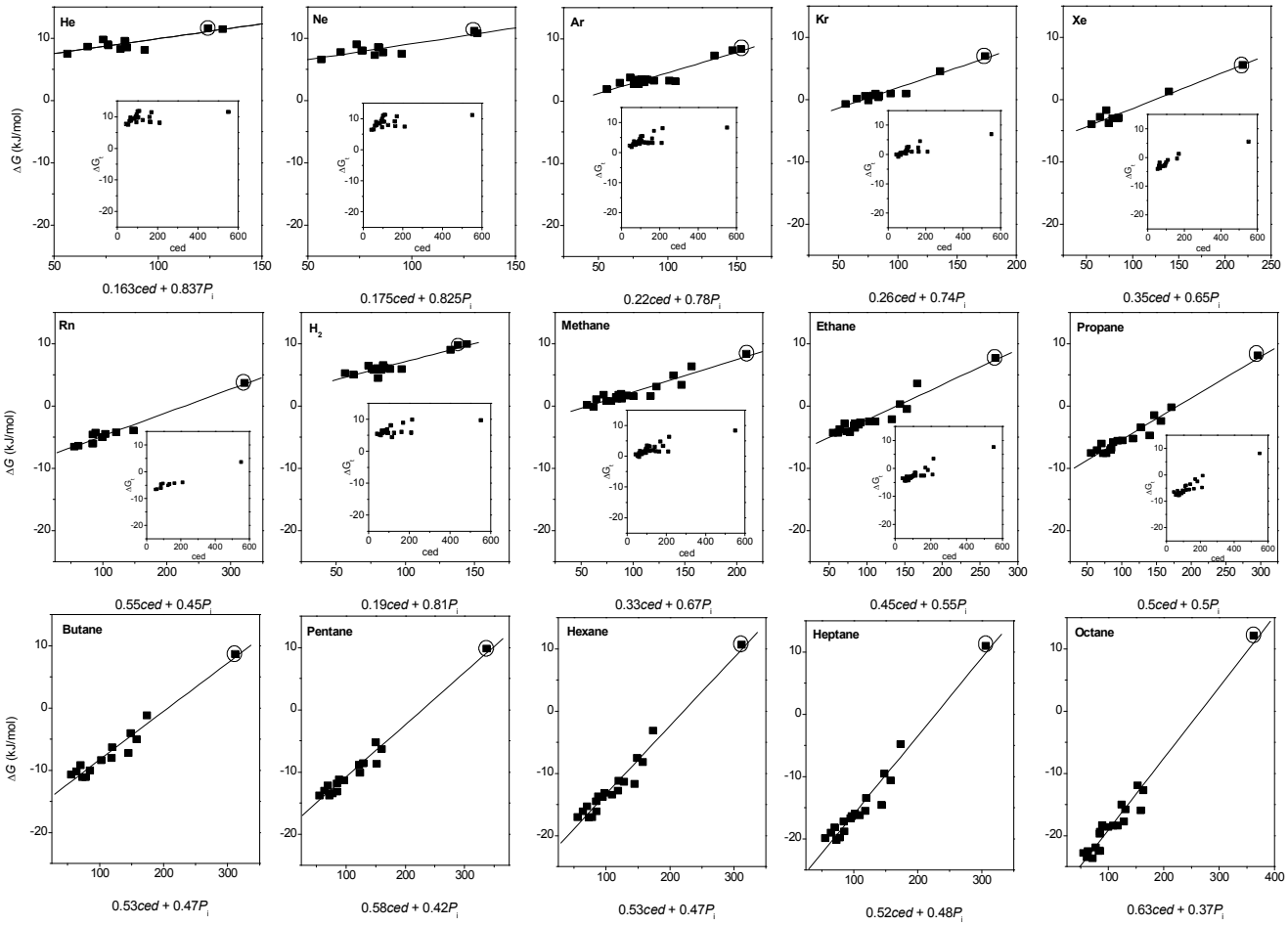


Figure S3. Re-analysis of the data in Figure 2 (main text) in which the data for water has been left out of the linear regression.

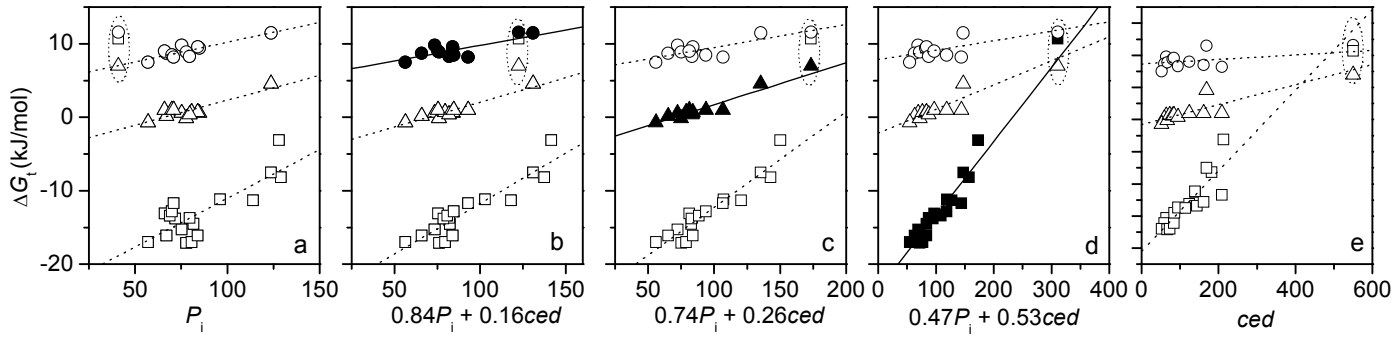
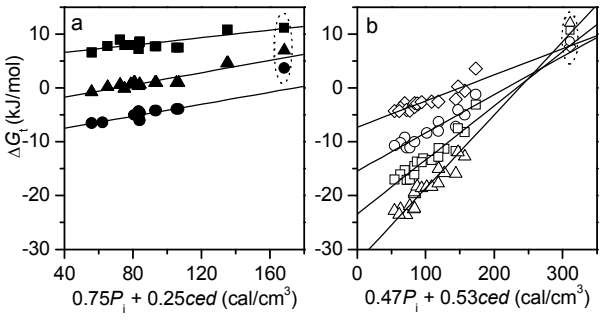


Figure S4. Re-analysis of the data in Figure 4 (main text) in which the data for water has been left out of the linear regression.



References:

S1: Allen, G.; Gee, G.; Wilson, G. J. *Polymer* **1960**, *1*, 456-466.